

## Solubility of Triazine Pesticides in Subcritical Water

Meredith S. S. Curren and Jerry W. King

Food Quality and Safety Research

National Center for Agricultural Utilization Research, ARS/USDA

1815 North University Street

Peoria, Illinois, 61604, U.S.A.

### Abstract

The solubilities of two triazine pesticides, atrazine and cyanazine, were determined in subcritical water. Solute solubilities were measured with a static solubility apparatus with on-line HPLC detection. Data was obtained at temperatures ranging from 50 to 125 °C. By increasing the temperature, the solubility of atrazine in water was increased 25-fold from its value at 50 °C, to a concentration of 1770  $\mu\text{g mL}^{-1}$  at 125 °C. The solubility of cyanazine increased an order of magnitude to a value of 2740  $\mu\text{g mL}^{-1}$  at 100 °C. The experiments were performed at a pressure of 50 bar in order to maintain the liquid state of water. The solubility of naphthalene in water was also measured to verify that the apparatus was functioning correctly.

### Introduction

In an effort to reduce the amount of hazardous organic solvents used in environmental monitoring, subcritical or "hot" water has been investigated as an alternative extraction agent over the past several years. Subcritical water is non-toxic, low in cost, and can be readily obtained. Water is also a convenient solvent as the sample does not have to be dried prior to extraction. In addition, the solute(s) of interest may be further analyzed while in aqueous solution, for example by immunoassay. Increasing the temperature of water has enabled the extraction of moderately polar and nonpolar organics from a wide variety of environmental matrices. Subcritical water has been used for the removal of PAH's and alkanes from contaminated soil, petroleum waste sludge, urban air particulate matter, and a spent catalyst; phenols, BTEX, and hydrocarbons from waste sludges; and PCB's from soil and sediment.<sup>1-5</sup>

The dielectric constant of ambient water is too high for the solubilization of most species of interest ( $\epsilon = 80$ ). However, its polarity is lowered by increasing the temperature. The solvent strength of water can thus be tuned for class selective extractions as mandated by the analyte polarity.<sup>1</sup> Supercritical water ( $T_c = 374$  °C;  $P_c = 221$  bar) has a low dielectric constant ( $\epsilon \approx 5 - 15$ ) and good solvating properties for relatively nonpolar organics, but its use is limited by its high temperature and pressure requirements, its potential reactivity, and its corrosivity.

Fortunately, water has modest polarities and attractive solvent properties at subcritical temperatures, that is, at temperatures up to the critical temperature. Although moderate pressures ( $> 40$  bar) are required to maintain the liquid state at these temperatures, pressure has only a small effect on the dielectric constant of water over the narrow pressure range required for subcritical extractions. Increasing the extraction temperature also has the dual effect of raising solute vapor pressures and improving the transport properties of solutes in the water.

Solubility data provide information on the important interactions between solute and solvent. These measurements aid in determining the solvent strength and system temperature which are required for conducting extractions using subcritical water. Although there is an abundance of solubility data in ambient water, only a few studies have investigated solute solubilities in subcritical water.<sup>6-8</sup> The solubilities of the triazine pesticides atrazine and cyanazine in subcritical water have been measured in this study. Atrazine is used to control broadleaf weeds and is currently one of the two most widely used agricultural pesticides in the U.S.. There is current concern about the potential cancer risks resulting from exposure to triazine pesticides. The solubility of propazine in subcritical water has been determined elsewhere.<sup>7</sup> The solubility of simazine is currently being investigated.

## Experimental

Static solubility measurements were performed with the apparatus shown in Figure 1.

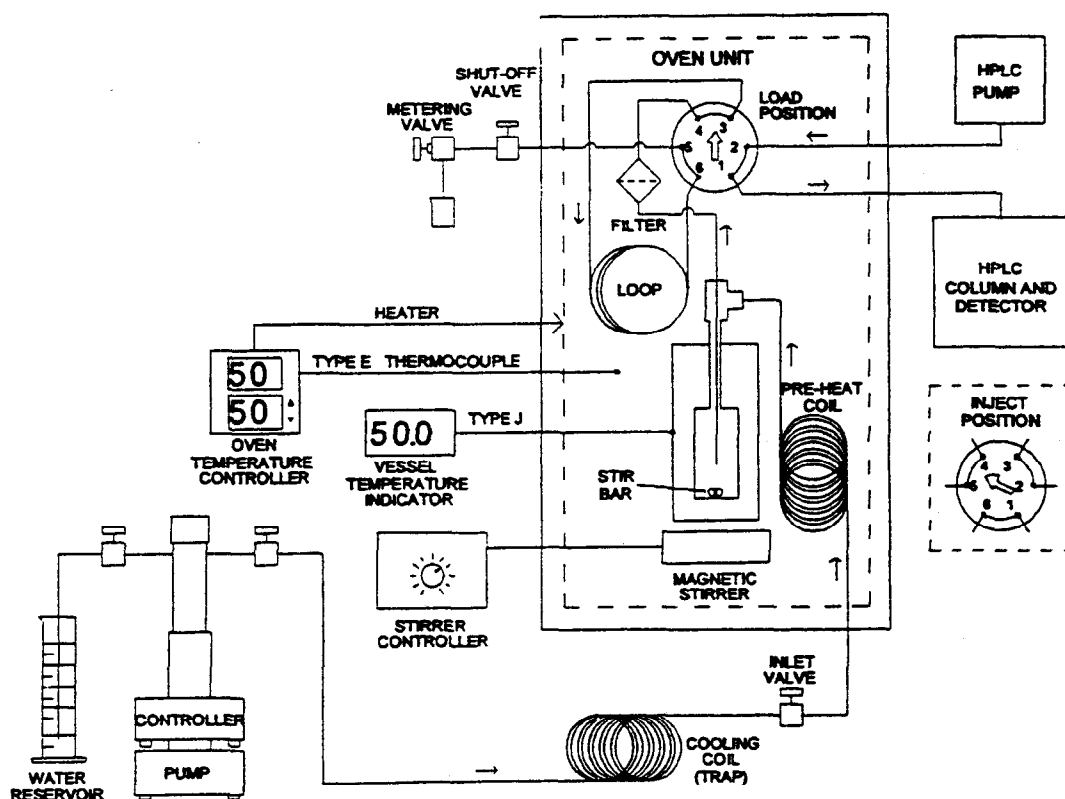


Figure 1: Solubility apparatus with on-line HPLC detection

The solubility apparatus is similar to one used for solubility measurements in supercritical carbon dioxide.<sup>9,10</sup> The apparatus is enclosed in a modified-Applied Separations Spe-ed oven for constant temperature control. Deionized water was delivered to a modified-Chemiquip stainless steel cell (30-31HF4GS) using an ISCO 100DX syringe pump set to maintain a constant pressure. As shown in Figure 1, the water first passed through a pre-heating coil in the oven. In addition, a cooling coil was placed in-line prior to this to prevent solute migration back to the pump. The cell contents were mixed with a magnetic stir bar driven by a Variomag MICRO remote stirrer. Sample aliquots were analyzed on-line with an HPLC. A Valco six-port valve was used for sampling. An in-line Valco filter with a 0.5  $\mu\text{m}$  frit prevented solid solute from entering the 2  $\mu\text{L}$  sample loop.

The HPLC mobile phase (75% HPLC-grade methanol / 25% deionized water) was delivered with a Beckman 114M solvent delivery module. The solutes were separated on a VYDAC reverse-phase C<sub>18</sub> column (25 cm x 4.6 mm; 0.5  $\mu\text{m}$ ). Detection of atrazine was made with an ISCO V4 UV absorbance detector (254 nm). Detection of cyanazine was accomplished with an SP8490 Thermo Separation Products UV detector (254 nm).

For solubility measurements, 10 – 30 mg of solute were placed in the cell. The cell was then charged with distilled, deionized water from the syringe pump. The cell contents were stirred until equilibrium was reached. The solute-saturated water was sampled by opening the shut-off valve with the six-port valve in the “load” position. A metering valve regulated the flow of effluent through the sample loop. The six-port valve was then turned to the “inject” position and the mobile phase delivered the sample to the HPLC system. Calibration curves were constructed using standards of appropriate pesticide concentrations prepared in both methanol and water.

## Results and Discussion

The solubility of naphthalene in subcritical water was first measured at several temperatures and pressures to ensure the apparatus was functioning correctly. These results are listed in Table 1 and are within reasonable proximity to the limited data already published in the literature.<sup>7</sup>

Table 1: Solubility of Naphthalene in Subcritical Water

Temperature ( $^{\circ}\text{C}$ )	Pressure (bar)	Solubility ( $\mu\text{g mL}^{-1}$ )	Reference <sup>7</sup>
25	1.013	$36 \pm 2$	$36 \pm 1$
26	40	$39 \pm 2$	$34 \pm 1$
35	40	$69 \pm 2$	$49 \pm 3$
50	70	$130 \pm 6$	$101 \pm 5$
65	30	$260 \pm 9$	$216 \pm 8$

By using a static solubility apparatus with on-line HPLC detection, we were able to avoid loss of the analyte upon sample collection. Solubility equilibria could be verified by varying the stirring

times (1 – 4 hrs) until there were no further increases in the measured solute solubility at each temperature. The stainless steel cell was carefully monitored for corrosion and no adverse effect was noted.

Solubility data for naphthalene was obtained at ambient temperatures at two different pressures, ambient pressure (i.e. ~1 bar) and 40 bar. The results indicate that pressure has a negligible effect on solute solubility over the narrow pressure range of interest for subcritical water extractions.

A similar result was observed during solubility measurements for atrazine in water (see Table 2). At 125 °C, the difference between the data obtained at 40 and 50 bar was not found to be significant.

Table 2: Solubility of Atrazine in Subcritical Water from 50 to 125 °C

Temperature (°C)	Pressure (bar)	Solubility ( $\mu\text{g mL}^{-1}$ ) <sup>a</sup>
50	50	70 $\pm$ 1
75	50	210 $\pm$ 2
100	50	500 $\pm$ 30
125	50	1780 $\pm$ 70
125	40	1770 $\pm$ 210

<sup>a</sup>Errors expressed as standard deviation (n = 3)

The solubility of atrazine in subcritical water increases 25-fold as the temperature is raised from 50 to 125 °C. This is largely due to the decrease in the dielectric constant of water, to about 55 at 125 °C. The increase in solubility can also be attributed to the positive effect of temperature on solute vapor pressure.

The pesticide cyanazine has higher solubilities in water than atrazine. The supportive data in Table 3 indicate the solubility of cyanazine increases 10-fold to a value of 2740  $\mu\text{g mL}^{-1}$  as the temperature is raised to 100 °C.

Table 3: Solubility of Cyanazine in Subcritical Water from 50 to 100 °C

Temperature (°C)	Pressure (bar)	Solubility ( $\mu\text{g mL}^{-1}$ )
50	50	290 $\pm$ 30 <sup>b</sup>
75	50	950 $\pm$ 50 <sup>c</sup>
100	50	2740 $\pm$ 80 <sup>d</sup>

Errors expressed as standard deviation (n = 5<sup>b</sup>, 4<sup>c</sup>, 3<sup>d</sup>)

Although atrazine has a higher vapor pressure, it appears that cyanazine forms stronger solute-solvent interactions at the moderate temperatures investigated in this study. Atrazine and cyanazine have the same basic structure, but the cyanazine molecule also contains a cyano

functional group. Cyanazine is therefore more polar and forms stronger hydrogen bonds with water.

The stability of each analyte in water was verified by GC-MS analysis of the saturated aqueous solutions after completion of the solubility experiments at the highest temperatures investigated. In addition, no absorbances other than the analyte peaks were observed on the chromatograms obtained during solubility experiments at all temperatures.

## Conclusions

The triazine pesticides atrazine and cyanazine are suited for subcritical water extractions as they are stable to hydrolysis, do not ionize at neutral or slightly acidic pH, and do not undergo thermal degradation at the temperatures reported in this study. As the temperature is increased to 100 °C (125 °C for atrazine), water becomes a better solvent for each of the analytes. This appears to be largely due to the decrease in the dielectric constant of water as the temperature is raised. The pesticide solubilities increase approximately 3-fold for every 25 °C increment. Although cyanazine is less volatile than atrazine, it has higher solubilities in subcritical water due to increased solute-solvent interactions.

The solubility data obtained in this study support the further development of a method to extract triazine pesticides from foods using subcritical water. Heating water to moderate temperatures will effect the removal of the atrazine and cyanazine, while current studies in our laboratory indicate co-extraction of matrix components is minimal.

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